



The effect of ammonia upon the electrocatalysis of hydrogen oxidation and oxygen reduction on polycrystalline platinum

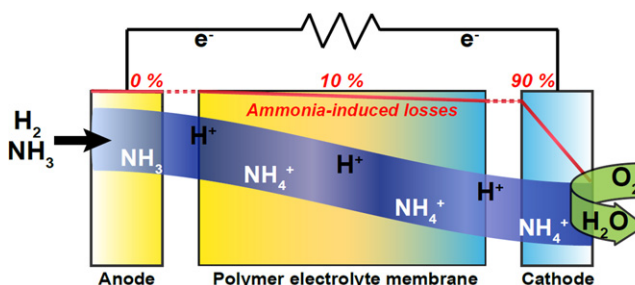
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HIGHLIGHTS

- ▶ Ammonia poisoning on the catalysis of fuel cell reactions on platinum.
- ▶ Study conducted in a rotating ring-disk electrode setup.
- ▶ No effects on hydrogen oxidation.
- ▶ Severe activity decrease for oxygen reduction.
- ▶ Cathode activity loss can explain most of the losses in a fuel cell.

GRAPHICAL ABSTRACT



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ABSTRACT

The influence of ammonium ions on the catalysis of hydrogen oxidation and oxygen reduction is studied by means of rotating ring-disk electrode experiments on polycrystalline platinum in perchloric acid. While ammonium does not affect the hydrogen oxidation reaction, the oxygen reduction reaction is severely poisoned. Poisoning at the cathode explains the majority of the losses observed in polymer electrolyte membrane fuel cells contaminated with ammonia. Voltammetry in deaerated solution suggest that the poisoning can be attributed to either ammonium oxidation or increased binding to OH species.

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1. Introduction

Polymer electrolyte membrane fuel cells (PEMFC) operated on hydrogen are an attractive zero-emission source of energy, providing that hydrogen is obtained from a renewable source. One of the main challenges fuel cells are facing is the transport, storage

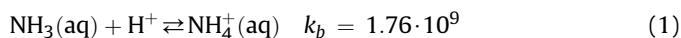
and subsequent release of the hydrogen [1,2]. Storing hydrogen in the form of ammonia could provide a solution to this problem [3–7]. Ammonia has a high storage density and its production is a mature well-established technology. Moreover, hydrogen sourced from cracked ammonia is free of CO [8], which would typically poison hydrogen oxidation at the anode of fuel cells [9]. Even so, it turns out that residual traces of ammonia in the hydrogen stream are detrimental to PEMFC performance, resulting in significant potential losses [10–13]. Not only can these trace contaminants be present in hydrogen produced by ammonia cracking, but also from

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hydrogen produced by steam reforming [10], if hydrogen is stored in metal hydrides containing nitrogen [14,15] or if it is obtained from ammonia boranes [16–19].

Regardless of the mechanism by which ammonia enters the hydrogen stream, it will quickly dissolve in the water in the membrane according to Henry's law. There ammonia will follow the ammonia–ammonium equilibrium (Eq. (1)), which, given the highly acidic environment, will be fully displaced toward ammonium ions [20]. These cations will be transported through the membrane to the cathode. A typical membrane diffusion time from anode to cathode is expected to be within 10–100 s [12].



Ammonia may potentially hinder fuel cell performance by poisoning either (1) the hydrogen oxidation reaction (HOR) at the anode, $\text{H}_2 \rightarrow 2\text{H}^+ + 2\text{e}^-$; (2) the proton channels in the Nafion® membrane, increasing its Ohmic resistance; (3) the oxygen reduction reaction (ORR) at the cathode, $\text{O}_2 + 4\text{e}^- + 4\text{H}^+ \rightarrow 2\text{H}_2\text{O}$.

Previous experiments on fuel cell setups have clearly established that the presence of ammonia is detrimental to PEMFC operation [10–13], even at concentrations as low as 1 ppm in the hydrogen stream. The increased resistance of the fuel membrane [21,22] can account for up to 10% of the increased losses in the presence of ammonia [11,12]. This would suggest that the majority of the losses are related to the catalysis of the HOR or ORR. Indeed, two recent rotating disk electrode (RDE) studies have confirmed that the ORR is poisoned in the presence of ammonia [23,24]. Halseid et al showed that the presence of ammonium significantly decreases the ORR activity of polycrystalline platinum catalyst in sulfuric acid solutions [23]. In a subsequent work, they also mentioned, as an aside, that a similar effect occurs in perchloric acid [25]. Very recently, Lopes et al reported a poisoning similar effect to Halseid et al., albeit on supported Pt/C catalysts, in perchloric acid solution, and in the absence of Nafion®. To the best of our knowledge, the hydrogen oxidation reaction has not been tested in the presence of ammonia.

Herein, we broaden the scope of earlier studies to evaluate the effect of ammonium on the catalysis of the HOR and ORR using a rotating ring-disk electrode setup in perchloric acid solution. By carrying out our studies in [weakly adsorbing] perchloric acid we more closely reproduce the conditions existing in a PEMFC than in studies conducted in [strongly adsorbing] sulfuric acid [26]. Moreover, by performing experiments with and without Nafion® at the electrode surface, we discern whether the poisoning reported in PEMFC's is influenced by its presence. The catalyst studied for both reactions is polycrystalline platinum, on the basis that its active site should resemble that of the platinum nanoparticles used in a fuel cell [27]. This enables us to look exclusively at the ammonium effects on the catalysis at a flat surface, avoiding the influence of the support. In summary, we establish whether the previously reported poisoning effects of ammonia are intrinsic to Pt, or related to the support or specific adsorption from the electrolyte.

2. Experimental

All glassware was cleaned for 48 h in a "piranha" solution consisting of a 3:1 v/v mixture of 96% H_2SO_4 and 30% H_2O_2 , followed by multiple heating and rinsing with ultrapure water (18.2 MΩ cm, TOC < 5 ppb) to remove sulfates. The electrochemical experiments were performed with Bio-Logic Instruments' VMP2 potentiostat, controlled by a computer. The rotating ring disk electrode (RRDE) assemblies were provided by Pine Instruments Corporation. A standard two-compartment glass cell was used, equipped with an

external jacket attached to a water bath with temperature control. The counter electrode was a Pt wire.

The electrolyte, 0.1 M HClO_4 (Merck Suprapur) was prepared with ultrapure water. The reference was a $\text{Hg}/\text{Hg}_2\text{SO}_4$ electrode, separated from the working electrode compartment using a ceramic frit. All potentials are quoted with respect to the reversible hydrogen electrode (RHE), and are corrected for Ohmic losses. Following each measurement, 0 V vs RHE was established by carrying out the hydrogen oxidation and hydrogen evolution reaction on Pt in the same electrolyte. The Ohmic drop was measured by carrying out an impedance spectrum with a peak-to-peak amplitude of 10 mV, typically from 500 kHz down to 100 Hz. The resistance was evaluated from the high frequency intercept on the horizontal (real) axis of the Nyquist plot and further checked by fitting the impedance spectra using EIS Spectrum Analyser software. Typically the uncompensated resistance came to ~30 Ω.

The pretreatment of the platinum polycrystalline electrode consisted of flame annealing for 2 min and subsequently cooling for 10 min under a stream of argon. It was then immediately covered by a drop of hydrogenated water to prevent contamination and assembled in the RRDE setup.

For the Nafion®-covered electrode experiments the same procedure was used to prepare the platinum polycrystal. After annealing and electrochemically cleaning the sample it was covered with 10 μL of 1:100 diluted Nafion® solution (Sigma–Aldrich) and dried under an argon stream prior to inserting it again into the electrochemical cell, as reported by Subbaraman et al. [28].

The RRDE was immersed into the electrochemical cell in Ar (Instrumental gas, AGA) saturated electrolyte. The potential was cycled between 0.05 and 1 V until a stable cyclic voltammogram was recorded to ensure a clean reproducible surface. The ORR activity measurements were conducted in an electrolyte saturated with O_2 (N55, AGA) by cycling the potential between 0 V and 1 V. The HOR measurements were obtained in an H_2 (N55, AGA) saturated electrolyte by cycling the potential between –0.02 V and 1 V. After obtaining a reference measurement in ammonia-free solution, 28 wt% ammonia solution (Sigma–Aldrich) was added to the electrolyte in the desired amount using a micropipette, reaching a final ammonia concentration ranging from 50 to 900 ppm (100 ppm = 0.006 M). Ammonia effects were immediate and stable throughout overnight measurements.

When adding ammonium into the solution the pH will be shifted depending on the quantity added (i.e. OH^- species introduced). We have taken such change into account by establishing the 0 V vs RHE at each ammonium concentration.

All the measurements have been repeated at least three times to ensure the reproducibility of the results.

The following equation (Eq. (3)) was used to obtain the kinetic current density for the ORR, where j_k is the kinetic current density, j_d the mass transfer limited current density and j the measured current density.

$$j_k = \frac{j \cdot j_d}{j_d - j} \quad (2)$$

The relative activity of the catalyst was defined as the fraction between ammonium-poisoned and ammonium-free kinetic currents, $j_{k,\text{NH}_4^+}/j_k$. It represents current decrease due to ammonia poisoning at a certain potential.

To compute the hydrogen peroxide yield the ring was potentiostated at 1.2 V, where the detection of peroxide is diffusion limited. Then Eq. (3) was used, where I_R is the current at the ring, I_D the current at the disk and η the collection efficiency, measured as a 20%.

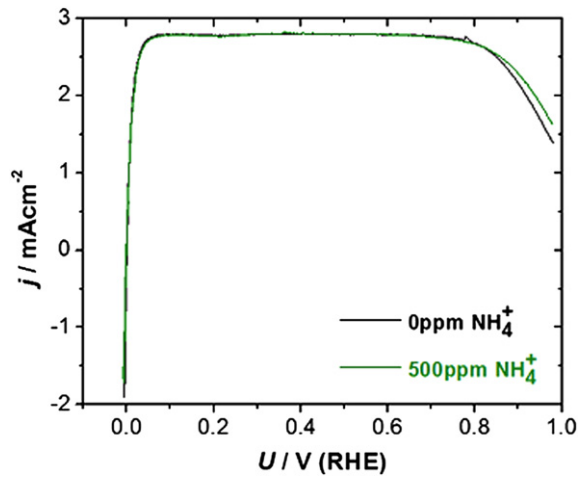


Fig. 1. HOR polarization curves with 0 (black) and 500 ppm of ammonium (green). Measurements at 10 mV s^{-1} and 23°C with a rotation speed of 2500 rpm in 0.1 M HClO_4 . Only the anodic sweep is shown. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

$$X_{\text{H}_2\text{O}_2} = \frac{2I_R/\eta}{I_D + I_R/\eta} \quad (3)$$

3. Results and discussion

3.1. Effects of ammonium on the hydrogen oxidation reaction

To study if ammonium ions may have any effect in the hydrogen oxidation reaction on polycrystalline platinum the electrolyte was saturated with H_2 and voltammetry was performed, with and without ammonium. As shown in Fig. 1, the HOR is unaffected by the presence of up to 500 ppm of ammonium. This is in agreement with results from the Japan Automobile Research Institute in a fuel cell setup where they do not observe any effect of Pt loading in the anode in the presence of ammonia [13]. We note that the HOR on Pt in liquid based acidic electrolyte is a very challenging reaction to study. The kinetics are so fast that mass transport limitations would dominate even at very low overpotentials or high rotation speeds [29–31].

Thus, it is conceivable that ammonium does actually have an effect at higher overpotentials, but it cannot be measured on a RRDE setup as the mass transfer limiting current is reached so quickly.

3.2. Effects of ammonium on the oxygen reduction reaction

The ORR activity in the presence of ammonium was measured by saturating the electrolyte with O_2 , as shown in Fig. 2b for the anodic cycle. Clearly, the presence of ammonium shifts the ORR toward higher overpotentials. The behavior is confirmed in the kinetic current plots shown in Fig. 2c, where mass transfer effects are eliminated. Notably, the decrease in activity brought about by the presence of ammonium is more pronounced at lower potentials, close to the potential window of operation of a PEMFC [32,33]. This is more clearly discernible from Fig. 2d, where the relative activity of the polycrystalline platinum electrode in the ORR for different ammonium concentrations is plotted, i.e. $j_{k,\text{NH}_4^+}/j_k$. The activity decreases with the ammonium concentration, as depicted in Fig. 3 at two selected potentials of 0.75 V and 0.9 V.

A similar, albeit more pronounced deactivation is observed in the cathodic cycle of the polarization curve, analyzed in Fig. 4b–d. This is in contrast with Halseid et al. results [12], who reported a stronger effect from ammonium on the anodic cycle. The reason for this discrepancy could be related to differences in the experimental conditions: apart from the fact that they carried out their experiments in sulfuric acid, they recorded the anodic sweep following a potentiostatic pretreatment at 0.2 V for 20 s, while the cathodic sweep followed a pretreatment of 20 s at 1.1 V.

The peroxide yield was as well measured in the presence of ammonium (Figs. 2a and 4a). The notion from previous reports [24,25] that ammonium increases peroxide formation is confirmed. However, we remark that the selectivity of the platinum polycrystalline electrode toward water formation is still close to optimal as no significant amount of hydrogen peroxide is produced, which would lead to accelerated membrane degradation [34].

We evaluate the influence of Nafion[®] on ammonium poisoning on the ORR. As shown in Fig. 5, the Nafion[®]-covered platinum polycrystalline activity decreases by a 17% at 0.9 V in the absence of ammonium, in agreement with Subbaraman et al. [28]. The Nafion[®] coating also introduced additional mass transport resistance (the diffusion limiting current decreased by a 10%) because it

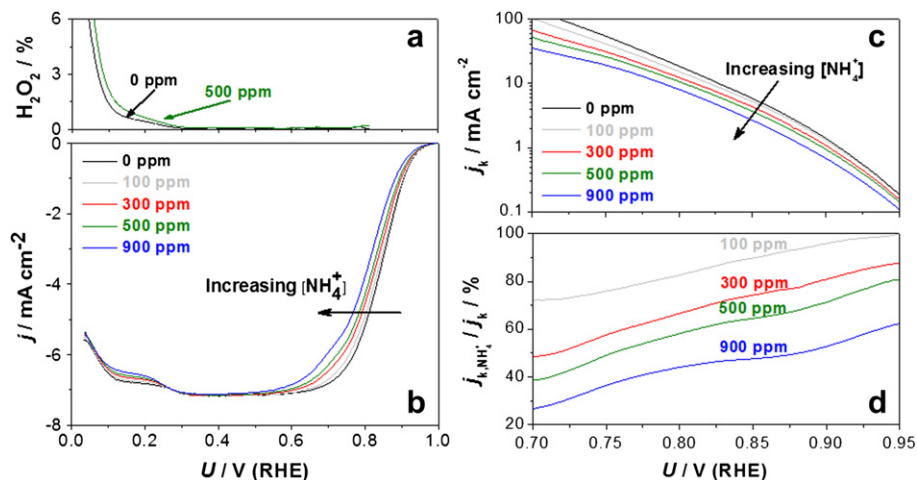


Fig. 2. Ammonia effects in the anodic cycle of the ORR. All the data was averaged over 3 independent measurements at 10 mV s^{-1} and 23°C with a rotation speed of 2500 rpm in 0.1 M HClO_4 . (a) Peroxide yield with 0 and 500 ppm of ammonium. (b) ORR anodic cycle polarization curves with increasing ammonium concentrations. (c) Kinetic current plot derived from the data in (b). (d) Platinum polycrystalline ORR relative activity against the applied potential.

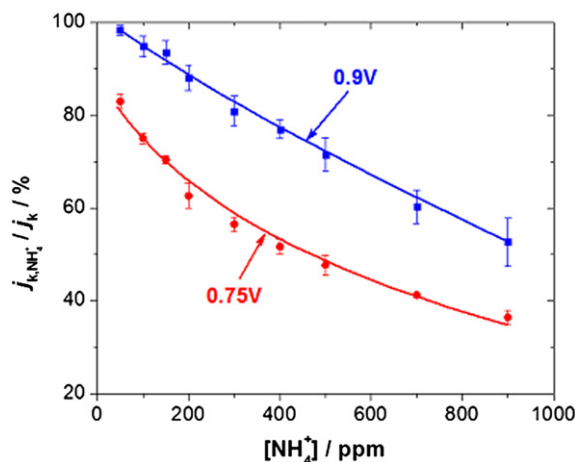


Fig. 3. Platinum polycrystalline activity decrease in the ORR for different ammonium concentrations at two selected potentials of 0.9 V (blue) and 0.75 V (red) for the anodic sweep. The lines serve to guide for the eye. The experimental conditions are the same as in Fig. 2. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

impediments oxygen diffusion to the electrode [28]. The presence of ammonium has a significant influence. Taking a concentration of 300 ppm of ammonium and at a potential of 0.85 V, the activity decrease is of 26% without Nafion[®], while with Nafion[®] the activity decreases as much as a 57% (relative to the Nafion[®]-covered electrode without ammonium). As the data already takes into account Nafion[®]-related losses, the increased poisoning suggests there may be a synergetic effect from the presence of both Nafion[®] and ammonia, as illustrated in the inset of Fig. 5. The diffusion limiting current remained unaltered upon ammonium addition, showing that the synergetic effect must be related to the catalysis of the oxygen reduction reaction.

3.3. Projected implications of current study on potential losses of a PEMFC

To illustrate the implications of our results, on Fig. 6 we estimate the effect of ammonia poisoning on a fuel cell. In the absence of more accurate data, we take a simple approach to quantify the

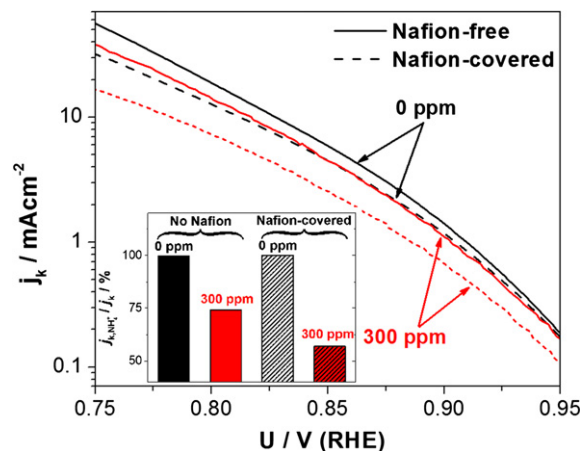


Fig. 5. ORR kinetic currents for Nafion[®]-free (solid lines) and Nafion[®]-covered (dashed lines) platinum polycrystalline electrodes. The lines without (black) and with 300 ppm of ammonium (red) are shown. In the inset, activity relative to Pt at 0.85V. Measurements taken at 10 mV s⁻¹ and 23 °C with a rotation speed of 2500 rpm in 0.1 M HClO₄ for the anodic cycle. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

potential losses in a fuel cell based on the results we have collected thus far.

In the absence of ammonia, the breakdown of the different components to the overpotential of a fuel cell is based on the analysis by Gasteiger and coworkers [9,26] using the same parameters as in [26].

On the basis of our results, we assume that ammonia poisoning does not influence the HOR, and that ammonia would not affect mass transport through the gas diffusion layer. We then assume that the exchange current density in the cathode decreases proportionally to the activity decrease at 0.75 V; in that way we can approximate how much poisoning at the cathode hinders fuel cell performance for a given ammonium concentration. In the figure we compute it for a concentration of 500 ppm, which would give approximately a 50% of activity decrease at 0.75 V. Taking into account that membrane resistance increase accounts at the most for a 10% of the ammonia-induced losses [11,12], we get a full picture of ammonia poisoning. As an example, at a cell potential of 0.7 V (horizontal gray line in Fig. 6) the current density decreases by

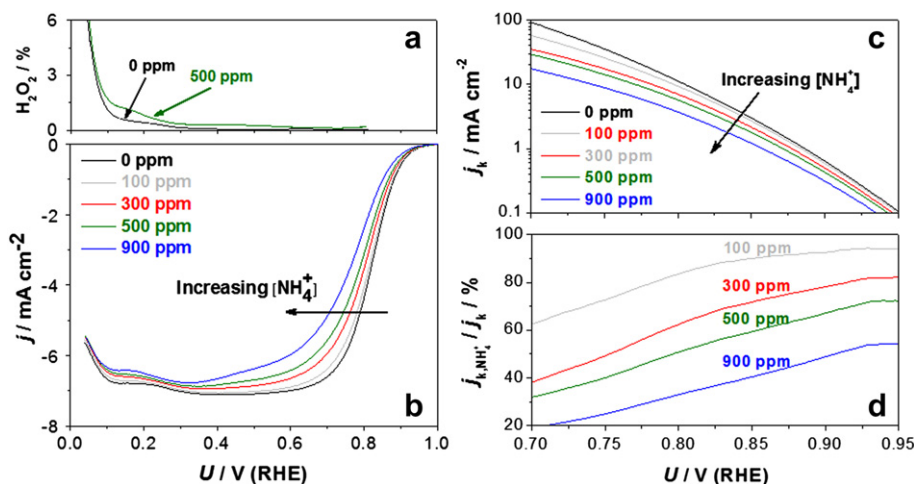


Fig. 4. Ammonia effects in the cathodic cycle of the ORR. All the data was averaged over 3 independent measurements at 10 mV s⁻¹ and 23 °C with a rotation speed of 2500 rpm in 0.1 M HClO₄. (a) Peroxide yield with 0 and 500 ppm of ammonium. (b) ORR cathodic cycle polarization curves with increasing ammonium concentrations. (c) Kinetic current plot derived from the data in (b). (d) Platinum polycrystalline ORR relative activity against the applied potential.

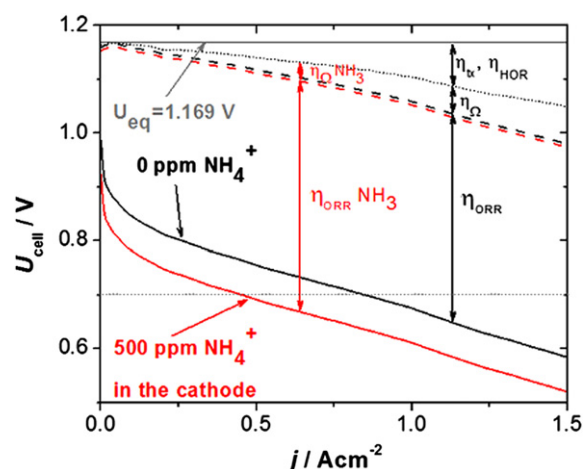


Fig. 6. Predicted effects of ammonia poisoning in a fuel cell based on measurements by Gasteiger et al. [26] (black) and from the current study (red). Resistance increase (η_{Ω}) accounts only for a 10% of the losses upon ammonium addition, while platinum activity decrease in the ORR (η_{ORR}) represents the remaining 90%. Mass transfer effects (η_{tx}) and hydrogen oxidation reaction (η_{HOR}) losses remain unaltered. U_{eq} represents the theoretical equilibrium potential for the overall fuel cell reaction. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

0.4 A cm^{-2} , implying that the power density will be reduced 50% from 0.56 W cm^{-2} to 0.28 W cm^{-2} .

Although the model is only a simple approximation, it provides an indication of how ammonia might degrade the performance of a fuel cell. More importantly, it seems to explain, at least qualitatively, the experimental results by other groups who observed significantly increased potential losses in a PEMFC [10–12]. Although the agreement between our simple model and those aforementioned studies at low to intermediate current densities, at high current densities it seems to underestimate the overpotential. This may be due to the deficiencies in the model arising from our RRDE experiments. Mass transport limitations prevent the kinetics of the ORR and HOR from being measured at high current densities, especially in the case of the HOR [29–31]. Consequently, should the effects of poisoning be more pronounced at high current densities for both reactions, they would not be measurable.

3.4. Effects of ammonium on the platinum surface

To investigate the reason for ammonium poisoning in the oxygen reduction reaction we performed cyclic voltammetry experiments in an argon-saturated solution from 0.05 V to 1 V at 50 mV s^{-1} (Fig. 7). This allows gathering information on the processes taking place at the electrode surface. We observe few changes in the hydrogen desorption region (marked as 1 in Fig. 7), while the hydrogen adsorption peaks are flattened (region 5), in agreement with the literature [12,35]. But it is the ORR region which presents several features of interest.

The presence of ammonium brings about an additional anodic peak at 0.75 V, (marked as 2) in the positive going scan, appearing upon ammonium addition which increases with increasing ammonium concentration. This also results in a corresponding change in the cathodic cycle (negative-going scan): the cathodic reduction peak at $\sim 0.8 \text{ V}$, labeled as 3, decreases in magnitude, whereas a new cathodic peak appears at $\sim 0.6 \text{ V}$, labeled as 4. Importantly, these peaks occur in the same potential range where poisoning is most pronounced during the course of the ORR. This could suggest that the cause of the poisoning for the ORR is related to the presence of these additional peaks.

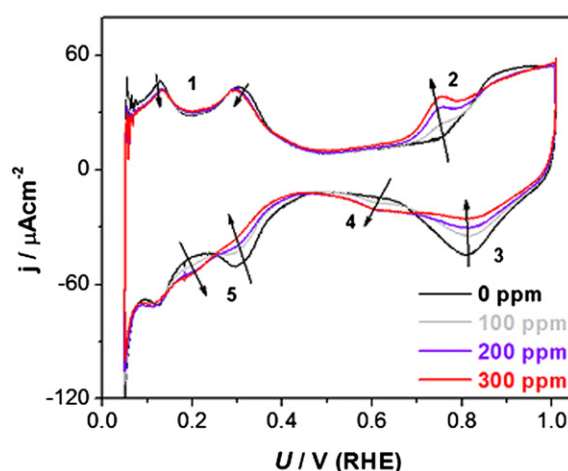


Fig. 7. Platinum polycrystalline voltammograms recorded in argon-saturated electrolyte. The arrows point toward changes upon addition of ammonium. Measurements taken at 23°C in 0.1 M HClO_4 with a sweep rate of 50 mV s^{-1} .

On the basis of the cyclic voltammograms in Ar, we propose two tentative hypotheses for the poisoning of the ORR in the presence of ammonium:

- The ammonium ion, or an N-containing adsorbate derived from ammonia acts as a site blocker, diminishing the number of sites available for the ORR. Such species would play a similar role to the sulfate or phosphate anions [36,37]. Ammonium may oxidize at the platinum electrode and produce NO, which would be a possible poison blocking the surface [38]. Although gas phase NO is not formed until potentials higher than 1.2 V [39], it is possible that it is formed as an adsorbate at lower potentials.
- An N-containing adsorbate derived from ammonium co-adsorbs with the adsorbed OH intermediates for the ORR, even if without significantly influencing their coverage. This co-adsorbed species would strengthen the binding of OH to the surface, therefore increasing the ORR overpotential. According to our current understanding of the ORR, the active sites are located on the terraces [27,40,41], where the (111) facet is predominant. In the potential region of interest for fuel cell applications ($< 0.9 \text{ V RHE}$), the surface is covered with up to $1/3$ a monolayer of OH, co-adsorbed with H_2O [42]. The OH is stabilized significantly by the surrounding water layer due to hydrogen bonds. This limits the rate of OH reduction to H_2O [43]. A strengthening of the binding to OH would difficult OH removal and difficult the overall oxygen reduction reaction [44,45]. N-containing species are also to form hydrogen bonds with H_2O or OH [46]. If these species were to co-adsorb with OH, replacing the H_2O , the binding of OH to the surface would be altered. The shift of the OH adsorption region in the voltammogram toward lower potentials may imply that OH binding to the surface is strengthened by an N-containing species, therefore explaining the ORR activity decrease.

4. Conclusions

We have studied the influence of ammonium on the hydrogen oxidation reaction (HOR) and the oxygen reduction reaction (ORR) on a polycrystalline platinum catalyst in perchloric acid solutions. While no poisoning was observed in the HOR, we show that ammonium hinders the catalysis of the ORR. The effects were stronger in the cathodic cycle, and more pronounced at lower potentials, approaching the potential window of operation of

a PEMFC. Experiments on Nafion[®]-covered electrodes showed additional poisoning, suggesting a synergetic effect by the presence of both ammonium and Nafion[®]. The specific reason for ammonium poisoning in the ORR could not be determined. Even so, base voltammetry in an inert gas saturated solution showed a clear modification of the surface condition under the potential range where the ORR takes place. We tentatively propose that an N-containing adsorbate may either be acting as a site blocker or modify the binding of the ORR intermediates to Pt. Both hypotheses could account for the poisoning of the ORR. On the basis of our data, we estimate the effect of ammonia to the total potential losses in a fuel cell and identify ammonium influence in the cathode as the main reason for the losses. Further studies are underway to (a) elucidate the fundamental cause of the poisoning of the ORR by ammonium and (b) on the basis of a, to develop strategies to mitigate these effects through improved catalysis.

Acknowledgments

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